The Bureau of Standards recently advised me that they did not know of any such publication, yet it seems that this would be one of the first requirements for a commercial change, and if it were now provided, might clear the way for the next step. The willingness of certain chemical manufacturers and dealers to furnish goods in metric quantities, does not amount to very much—it is easily done, and has been done automatically since the demand appeared, but a few more practical suggestions with the necessary tools (such as conversion tables as above) would greatly smooth the way in the eyes of the average business man, who is probably accounted the greatest opponent of the change.

HENRY PAUL BUSCH

CONCERNING THE ARTICLE "A NEW GRAPHIC ANALYTIC METHOD

IN an article entitled, "A New Graphic Analytic Method," in SCIENCE of October 7, 1921, Mr. R. von Huhn states a method of deriving the graph of a special case of a function of a function. Stated in more usual mathematical terms:

Given the curves that represent

$$y = kx + m,$$
$$z = hy + n,$$

the curve that represents the resulting equation

$$z = lx + q$$

is drawn.

Essentially the same method, in a far more general form, and in a more usual mathematical formulation has been given by several mathematicians. See the articles by E. H. Moore, "Cross-section paper as a mathematical instrument," in *The School Review*, May, 1906, and by A. Kempner, "Some hints on plotting graphs in analytic geometry," in *The American Mathematical Monthly*, Vol. XXIV, pp. 17-21, and, in particular, the more specific article by W. H. Roever, "Graphical constructions for a function of a function and for a function given by a pair of parametric equations," in "*The American Mathematical Monthly*, Vol. XXIII, pp. 330-333. E. R. Hedrick has suggested the modification of transferring points from one of the two like-named axes to the other by means of a 45° triangle and he has also emphasized the geometric interpretation of the operation as that of finding the projection on the plane xy of the intersection of the two cylindrical surfaces

$$F(x, y) = 0, \qquad \Phi(y, z) = 0$$

This perfectly general problem was well-known to mathematicians and hence the special case treated in the article mentioned above can not be regarded as novel.

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SPECIAL ARTICLES

THE PROPERTIES OF ELEMENTS AND SALTS AS RELATED TO THE DIMENSIONS OF ATOMS AND IONS[1]

(An Application of Geometry to the Study of Inorganic Chemistry)

RECENTLY great interest has been aroused in connection with the determination of the dimensions of atoms and ions by various methods; particularly that of X-ray crystal analysis,—by Bragg, Landè, Hull, Davey, and others. Very recently Fajans and Grimm, and later Biltz and also Henglein have pointed out that there is a very simple linear relation between the volume of certain series of salts and the atomic volumes of their constituents. Six years ago Professor W. D. Harkins and the writer began work upon what are known as complex chemical compounds, such as ammines and hydrates, in an attempt to show *that a large number of the properties of these compounds, as well as those of simple salts, are very simply related to the sizes of the atoms, atomic groups, and ions, from which the salts are built.* This point of view has now been developed in considerable detail by the writer. *The simplicity of the relation is apparent when it is realized that for a number of groups in the periodic system of the most common elements, as many as 35 properties of their simple compounds have been found to be related in a linear way to the atomic and ionic volumes of*

[1] From an address presented at the University of Chicago in December, 1921, and to the Harvard-Technology Chemical Club in January, 1922.

their constituents, as will be shown later in detail.

The present paper will be limited to a consideration of these relationships in the case of the elements and simple compounds, and will indicate briefly some of the most interesting of a large number of cases which show the above simple relationship.

While the writer was working upon the more extended and general set of relations given in this letter, the above mentioned paper by Biltz appeared. In this he exhibited the volume relations which may be used as a basis for the general discussion. Biltz found that if the atomic volumes of certain of the noble gases (argon, krypton, and xenon) are plotted along one axis in a two dimensional plot, the atomic volumes of the three corresponding halogens give one straight line, the three alkalies another, the three members of group 4B another, and the three members of group 4A, a fourth straight line; while in all of the other groups there is a departure from linearity. It may be noted that the alkali and halogen groups on the one hand, and groups 4 A and B on the other, are equidistant from the group of the rare gases of the atmosphere in the periodic table of the elements as represented by Harkins and Hall. The facts found in this work are beautifully in accord with what might be expected from this particular model of the periodic system.

The relations found by the writer are much more general than those given in the preceding paragraph. *Thus it is found that if the atomic volumes of the five alkali elements are plotted on one axis* (as the X-axis) *of a three dimensional rectangular coordinate system the atomic volumes of the four halogens on the Z-axis, and the molecular volumes of the alkali halides on the Y-axis, practically all of the points (all except some of those for cæsium), lie quite nearly on a plane* $z = bx + cy + d$ *which passes nearly through the origin.* Thus the relationship is very much more simple than has heretofore been suspected.

It is even more remarkable that when instead of the molecular volumes of the salts, other properties are plotted on the Y-axis, it is found that *in a very large number of cases* the surface, while not a plane, is of the extremely simple form known as a *doubly ruled surface.* Commonly the surfaces found may be expressed by the equation $z = axy + bx + cy + d$. For the molecular volumes of the alkali halides, the following expression, in which z is the molecular volume, x the atomic volume of an alkali metal, and y the atomic volume of a halogen, holds rigorously: $z = .0074xy + .3655x + y - 9.07 = .00849xy + .3345x + .9442y - 7.49$.

Since it is difficult to present the characteristics of these remarkable doubly ruled surfaces in a very simple way, the discussion of the present paper will be given in terms of the projections of these surfaces on the various coordinate planes. Simply to present one example, the two dimensional plot for the halogens may be considered. If the atomic volumes of the four members of the halogen group, fluorine, chlorine, bromine, and iodine, are plotted along one axis of a plane rectangular coordinate system, and along the other any of a large number of properties of other groups of elements, of other properties of the halogens themselves, and of compounds in which they are substituents, perfectly linear relationships are found, for which simple equations may be derived and calculations made with which reputable experimental data agree quite accurately. Some of these properties linear to the *halogen atom dimensions* may be briefly enumerated as follows: atomic volumes, atomic radii, viscosities or boiling points of the rare gases; atomic volumes of the alkali metals and alternate members of group 4; *for the elementary halogens,* the molecular diameters, melting points, boiling points, critical temperatures, latent heats of fusion and vaporization, normal potentials, cubical coefficients of expansion, atomic frequencies, magnetic susceptibilities, cohesional dimensions, $\sqrt{a}$ and b of van der Waals' equation, and the heat of formation of ions from the elements; *for the hydrogen halides,* the molecular volumes and diameters, boiling points, melting points, critical temperatures, latent heat of vaporization and the energy of ionization; *for organic compounds,* the atomic volumes of the halogens in combination, the atomic refraction for the D

TABLE I.
Atomic and Ionic Radii ($\times 10^8$) for the Halogens.

	Bragg[2]	Davey[3]	Rankine[4]	Landé[5]	Grimm[5]	Schwendenwein[5]	Richards[6]	Henglein[7]
F—		1.13			0.75	0.99		0.8525
Cl—	1.06	1.56	1.27	1.60	0.95	1.232	1.40	1.00
Br—	1.19	1.73	1.35	1.80	1.02	1.312	1.55	1.066
I—	1.40	1.98	1.49	2.10	1.12	1.432	1.70	1.179

line, and the molecular volumes of numerous halogen-substituted compounds; *for salts,* the molecular volumes of practically all metal halides, the volume change in solution, the melting points, boiling points, latent heat of vaporization, heat of formation and specific compressibilities of the alkali halides and many others, the percentage contraction for halides of small cations, the distance between the centers of oppositely charged ions in crystals, and the radii of ionic halogens.

There are many interesting details of each item in the above enumeration of which space does not admit detailed consideration. For example the percentage contraction undergone when a salt is formed from the free elements, is found in this work to be related in a *fundamental* way to the *properties of the complex compound* formed from it. Thus when a nickel halide is formed by the union of nickel with any of the halogens (fluorine, chlorine, bromine, or iodine) the percentage contraction is the same (22.5 per cent.) in each of the four cases. In the case of the cobalt and cupric halides the magnitude of the contraction is not quite constant, but increases slightly from the fluoride to the iodide. The constancy of the percentage contraction is also found when any halogen is combined in turn with the alkali metals (lithium, sodium, potassium, and rubidium). The contraction amounts to 60 per cent. each for the four fluorides, 43 per cent. each for the four chlorides, 38 per cent. each for the four bromides, and 30 per cent. for the four iodides. It is seen that the relative contraction decreases with increasing number of non-nuclear electrons in the halogen atom. The contraction for the cæsium halides is greater than that given above for the other alkali halides. However in the oxy-acid salts cæsium shows the same contraction as the other salts of the alkalis, and in *molten halides* it is also *perfectly normal* as indicated by the careful researches of Jaeger. The anomaly of cæsium is therefore to be attributed to difference in crystal form. As a matter of fact cæsium halides possess cube-centered lattices, while all other alkali halides are simple cubic.

The ionic radii can be derived from experimentally determined crystal distances only by means of some assumption. The following table shows the widely varying values, multiplied by 10^8, which have been presented by eight workers.

It is a *singular fact that in spite of the wide discrepancies all of the values except those of Richards are quite accurately linearly related to the atomic volumes of the halogens at the boiling point,* showing that whatever basis of calculation may be the closely similar halogens are still related to each other in relatively the same way. Richards' values are calculated from the atomic volumes of chlorine, bromine and iodine at 25° where the three values are practically coincident, and this may explain the deviations in this case. However the *third powers* of the radii values, as direct functions of the volumes of single combined atoms, are found to be linearly related to gram-atomic volumes. This is apparently of greater signifi-

[2] From close-packing in crystals.

[3] From equality in size of ions with same number of external electrons: $K^+ = Cl^-$, $Rb^+ = Br^-$, $Cs^+ = I^-$.

[4] From viscosity of gaseous halogens, hence radii of atoms.

[5] From various aspects of Bohr theory. Represents actual distance from nucleus to outermost electron orbit.

[6] From extrapolation of compressibility-contraction curve to zero compressibility.

[7] From empirical considerations of linearity to molecular volumes, *Zeit. anorg. allgem. Chem.*, 120: 77 (December 14, 1921).

TABLE II
Atomic and Ionic Radii ($\times 10^8$) of the Alkali Elements[10]

	Bragg	Davey	Landè	Grimm	Schwen-den-wein	Richards			Saha[9]	Heng-lein
						Chlo-ride	Bro-mide	Iodide		
Li	1.50	0.98	0.88		0.50	1.15	1.20	1.30	1.34	1.00
Na	1.75	1.25	1.15	0.52	0.65	1.45	1.45	1.55	1.41	1.428
K	2.10	1.56	1.45	0.79	0.948	1.75	1.75	1.85	1.67	2.108
Rb	2.25	1.73	1.60	0.91	1.128	1.90	1.90	1.95	1.73	2.478
Cs	2.35	1.78	1.60	1.01	1.32	1.90	1.85	1.90	1.86	

cance that the chance linearity of *first powers.* The most recent values are those of Henglein, whose procedure is very questionable inasmuch as he takes Fajans' values for bromide and iodide ions and then *assigns values* to chloride and fluoride so that a straight line connects the molecular volumes of the halides of any alkali metal and the sizes of the substituent halogen ion. By using the same process for determining the sizes of the alkali ions it is of course possible at once to write an equation by which the molecular volumes may be calculated from the *constant size* of the ion. Henglein quite naturally observes a very good agreement between calculated and experimental values.

Table I indicates the definite progression in size and properties from one member to the next in such nearly perfect[8] families (or groups) of elements as the halogens and the alkalies.

It is interesting in this connection to compare the radius of the ammonium ion. Using the distance between ion centers found by Bartlett and Langmuir for the ammonium halides, and subtracting the radii of the halogen ions, the ammonium ion is found to have a radius of 1.90×10^{-8} cm., if Richards' values are used, or 1.76×10^{-8} with Davey's. In either case this is also the radius of the rubidium ion. That this equality is extended to the molecular volumes and other properties of both simple and complex ammonium and rubidium salts may be shown by numerous examples.

From the above considerations it is at once apparent that, by plotting the various properties of the halogens, *both free and combined,* which are linear to the dimensions of the halogens, a large number of possible new linear relationships may be predicted. It has never before been possible to ascribe such perfect and simple constancy and dependency of essentially all properties upon one fundamental variable of matter. The definite increase in size in passing from fluorine to chlorine to bromine to iodine atoms is paralleled in a linear fashion not only by all dimensions of the atom free or in combination, neutral or charged, but by practically every measurable property. That this extends even to variations in the electromagnetic stray fields which determine the strength of secondary valence forces and complex salt formation, will be indicated in a following paper.

Exactly as has been done with the halogens, the various properties of the alkali metals, free and combined, may be related. The ionic radii have been variously calculated as follows: These values (with the exception of those of

[8] According to the periodic table of Harkins and Hall the two groups of elements nearest the group of rare gases, that is the alkali and halogen groups, should be the ones in which linear relations may be expected to hold for practically all of the elements in the group. Such groups may be designated as "perfect." In this sense groups 2 to 6 inclusive are imperfect, since a considerable break in properties occurs between the second and third elements in each of these groups.

[9] From ionization potentials.

[10] Other values are those of Born from heats of hydration, Pleyer-Wegau from diffusion of metals in mercury, Stokes-Born from ion mobilities, Gunther-Schulze from volume changes in permutites and from polarization capacities, and Heydweiller from ion refraction.

Richards) are related in a linear way to many of the properties of the elements and their salts.

From the average of the most logical values of the effective radii of atoms and ions of the alkali metals and the halogens it is found that the space functions of the third powers of the radii are as follows: for halogen ions, φ_0 (ratio of cube of radii $\times$ 6.063 $\times$ 10^{23} to gram-ionic volume) $= .44$; for halogen atoms, $\varphi_0 = .25$ (agreeing with van der Waal's postulate); for alkali ions, $\varphi_0 = .25$; and for alkali atoms, $\varphi_0 = .52$. In other words the volume of the halogen ion is roughly 44-25 that of the atom, and the alkali ion 25-52 of the corresponding atom. Upon this simple basis the molecular volumes of the alkali halides are found to be dependent as $3.35 \times 10^{24}(r^3_{\text{hal·ion}} + 1.76r^3_{\text{alk·ion}})$.

Finally there are many linear relationships to be found among the other elements: *e. g.*, the molecular volumes of the cuprous, silver and thallous halides and the *stability of the triammines* of these halides, to the atomic volumes or ionic sizes of cuprous copper, silver and thallium; the atomic volumes of calcium, strontium and barium (in some cases also lead), to the molecular volumes of practically any alkaline earth salt, or the stability of the hexammines of the metals (*e. g.*, Ca. 6 NH_3) to the ionic sizes of the alkaline earths; the molecular volumes of various sulfides, selenides and tellurides to the size of sulfide, selenide and telluride ions; the molecular volumes of the oxides to the atomic volumes of titanium, zirconium and cerium; and numerous linear relationships between the molecular volumes, stability, percentage contraction and heats of dissociation of complex compounds and the molecular, atomic and ionic dimensions of the constituents of the whole complex molecule. These will be considered in a separate paper.

The general method of representing the properties of salts as functions of the dimensions of their constituent ions (or of the atomic volumes of the constituent elements) is of such fundamental importance that an extensive study of the characteristics of these surfaces is now being made in collaboration with Professor A. C. Lunn and Professor W. D. Harkins of this university. As has been stated some of these *surfaces* are *planes,* while most of the others are *doubly* ruled.

GEORGE L. CLARK

UNIVERSITY OF CHICAGO,
FEBRUARY 3

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

SECTION L (1) HISTORY OF SCIENCE

THE History of Science section was organized on a temporary basis at the Chicago meeting of the American Association for the Advancement of Science, December, 1920. At the Toronto meeting, December, 1921, it was formally organized, and recognized by the Council of the American Association for the Advancement of Science as a sub-section in Section L (Historical and Philological)

This step now assures the future of the History of Science movement in the United States. The movement has been growing steadily, not alone in active interest and research by various scholars, but by the fact that our colleges, universities and technical schools are taking cognizance of its place in the curriculum of science and technology.

If we are, at all, to enter a new epoch of science teaching, and give more emphasis to the humanistic element in our sciences, it is evidently time now to consider the matter. Science, that which we love to call pure science, has been too long dominated by the ulterior motive of materialism.

The fact that the American Association for the Advancement of Science has recognized the value and purpose of History of Science, and accorded it a place in its comprehensive activities, indicates a step forward, not alone in the "Association" progress, but in science, and in educational methods as well.

A movement that can be fostered by two large and widely different organizations, such as the American Historical Association and the American Association for the Advancement of Science, is doubly assured of success and future stability, in relation to other intellectual movements.

The Toronto meeting was in charge of a local